



Energy, Mines and
Resources Canada

Énergie, Mines et
Ressources Canada

CANMET

Canada Centre
for Mineral
and Energy
Technology

Centre canadien
de la technologie
des minéraux
et de l'énergie

ELECTRODES FOR SOLID-STATE ELECTROLYTE FUEL CELLS - ELECTRODE MORPHOLOGY

J.D. Canaday, A.K. Kuriakose, A. Ahmad, and T.A. Wheat
Ceramic Section
Mineral Processing Laboratory

October 1983

This document is a report
of the work done for the
purpose of and is
for the use of the
reporting on the
requirements of the
the opinion of the
to Mineral and Energy
(CANMET)

Ce document est un rapport
de la recherche et rédigé
pour le but de
pour la documentation
la représentation nulle-
l'opinion de
pour les minéraux et de
(CANMET)

Project ERP-4.5.5.0.53
Hydrogen-Air Fuel Cell Project

FEB 26 1984
MICROMEDIA

31pp

MINERALS RESEARCH PROGRAM
MINERAL SCIENCES LABORATORIES
DIVISION REPORT ERP/MSL 83-134 (IR)

This document is a report
of the work done for the
purpose of and is
for the use of the
reporting on the
requirements of the
the opinion of the
for Mineral and Energy
(CANMET)

Ce document est un rapport
de la recherche et rédigé
pour le but de
pour la documentation
la représentation nulle-
l'opinion de
pour les minéraux et de
(CANMET)

ELECTRODES FOR SOLID-STATE
ELECTROLYTE FUEL CELLS -
ELECTRODE MORPHOLOGY

by

J.D. Canaday*, A.K. Kuriakose*, A. Ahmad*, and T.A. Wheat*

ABSTRACT

Electrode morphology models, parameters, and measurement methods are discussed. Fuel cell electrodes are shown to have properties similar to thin-film devices and catalytic structures. Morphology studies of electrodes used with the ZrO_2 -type electrolyte are reviewed and investigations relevant to protonic-electrolyte fuel cell electrodes are recommended.

*Research Scientist, Ceramic Section, Mineral Processing Laboratory,
Mineral Sciences Laboratories, CANMET, Energy, Mines and Resources Canada,
Ottawa.

ÉLECTRODES POUR PILES À COMBUSTIBLE À ÉLECTROLYTE
SOLIDE, FORMÉ DE L'ÉLECTRODE

par

J.D. Canaday*, A.K. Kuriakose*, A. Ahmad*, et T.A. Wheat*

RÉSUMÉ

L'article traite de modèles, de paramètres et de méthodes de mesure relatifs à la forme d'électrodes. On montre que les électrodes pour piles à combustible ont des propriétés semblables à celles des dispositifs à pellicule mince et des structures catalytiques. On fait la revue des études sur les formes des électrodes à électrolyte du type ZrO_2 , et on recommande de faire les recherches pertinentes sur les électrodes à électrolyte protonique pour piles à combustible.

*Chercheur scientifique, Section de la céramique, Laboratoire de traitement des minéraux, Laboratoires des sciences minérales, CANMET, Énergie, Mines et Ressources Canada, Ottawa.

CONTENTS

	Page
ABSTRACT	1
RÉSUMÉ	11
INTRODUCTION	1
MORPHOLOGY MODELS	2
ELECTRODE PROPERTIES	5
Morphological Parameters and Measurement Methods	5
Thin-Film Porosity Measurements	5
Thin-Film Surface Area Measurements	10
Properties of Thin Film Catalysts, and Fuel Cell Electrodes	13
Electrodes for ZrO ₂ -Type Cells	15
Electrodes for Protonic Electrolyte Fuel Cells	21
SUMMARY AND CONCLUSIONS	23
REFERENCES	24

TABLES

1. Electrode morphology characteristics	5
2. Porosity of thin films	7&8
3. Pore diameter of thin films	9
4. Specific surface area of thin films and catalysts	11
5. Comparison of thin film, catalyst and electrode requirements	14
6. Electrodes for ZrO ₂ -type fuel cells	16,17, 18,19,20,21
7. Suggested electrode studies for protonic electrolytes	23

FIGURE

1. Schematic view of protonic fuel cell electrode porosity and the three-phase-line model	3
---	---

INTRODUCTION

Theoretical (1) fuel-cell efficiencies in the range of 80-90% are reduced in the real device (2) to approximately 50%. This loss can be attributed in part to ohmic polarization occurring within the electrolyte. In addition to this mechanism, polarization at the electrolyte-electrode interface and within the electrode structure also result in a decrease of cell voltage and a corresponding loss of efficiency.

Numerous physical and chemical processes are involved in the generation of fuel-cell electricity. Fuel and oxidant gases, H_2 and O_2 for example, diffuse because of concentration gradients through the anode and cathode respectively towards the electrolyte-electrode interfaces. These diffusion processes result in concentration polarization. In the interfacial regions, charge transfer reactions involving catalytic steps occur, which produce activation polarization.

The transport of mass and charge is related in a complex manner to the structure of the electrode. This structure, or morphology, can be defined by measurable quantities such as thickness, porosity, and specific surface area.

The purpose of this report is to discuss the morphological aspects of solid electrolyte fuel cell electrodes. Morphological parameters will be defined, and methods for their measurement will be given. Porosity and surface area properties of thin films will be presented. It will also be shown that electrodes have characteristics similar to thin-film and catalytic devices. Morphology studies of ZrO_2 fuel cell electrodes will be compared. From these considerations, guidelines for the development of protonic solid electrolyte protonic electrodes will be given.

MORPHOLOGY MODELS

Performance characteristics of ZrO_2 fuel cells have been summarized (3-5), and these studies showed that the polarization mechanisms depend on the electrode composition, deposition method, and morphology.

Figure 1 shows a simplified schematic diagram of two possible electrode pore structures and the three-phase-line model (6-8) for a protonic-electrolyte fuel cell. A micropore structure, as often found with thin-film electronic devices, does not permit a fast rate of gas diffusion, which would be the case for open or connected pores. Electrode morphology has been described theoretically by the three-phase-line model. This line represents the region in which the electrode, electrolyte, and gas are in mutual contact. A two-phase boundary is formed at the electrode-electrolyte interface. The dissociation and ionization of hydrogen and oxygen molecules are also illustrated. Protonic ions, e.g., H_3O^+ , are depicted as migrating through the solid electrolyte while the circuit is completed by the flow of electrons through the external load resistance.

Various adsorption, dissolution, and diffusion processes have been associated (9-11) with fuel and oxidant species in solid-electrolyte fuel cells. These processes can be summarized for the electrode, electrolyte, and interface as follows:

Electrode

- a) Gas diffusion through electrode pores.
- b) Adsorption and dissociation of species on electrode particle surfaces.
- c) Surface diffusion of adsorbed species on electrode particles to three-phase boundary.
- d) Dissolution of adsorbed species into electrode particles.
- e) Bulk and/or grain boundary diffusion of dissolved species in electrode particles.

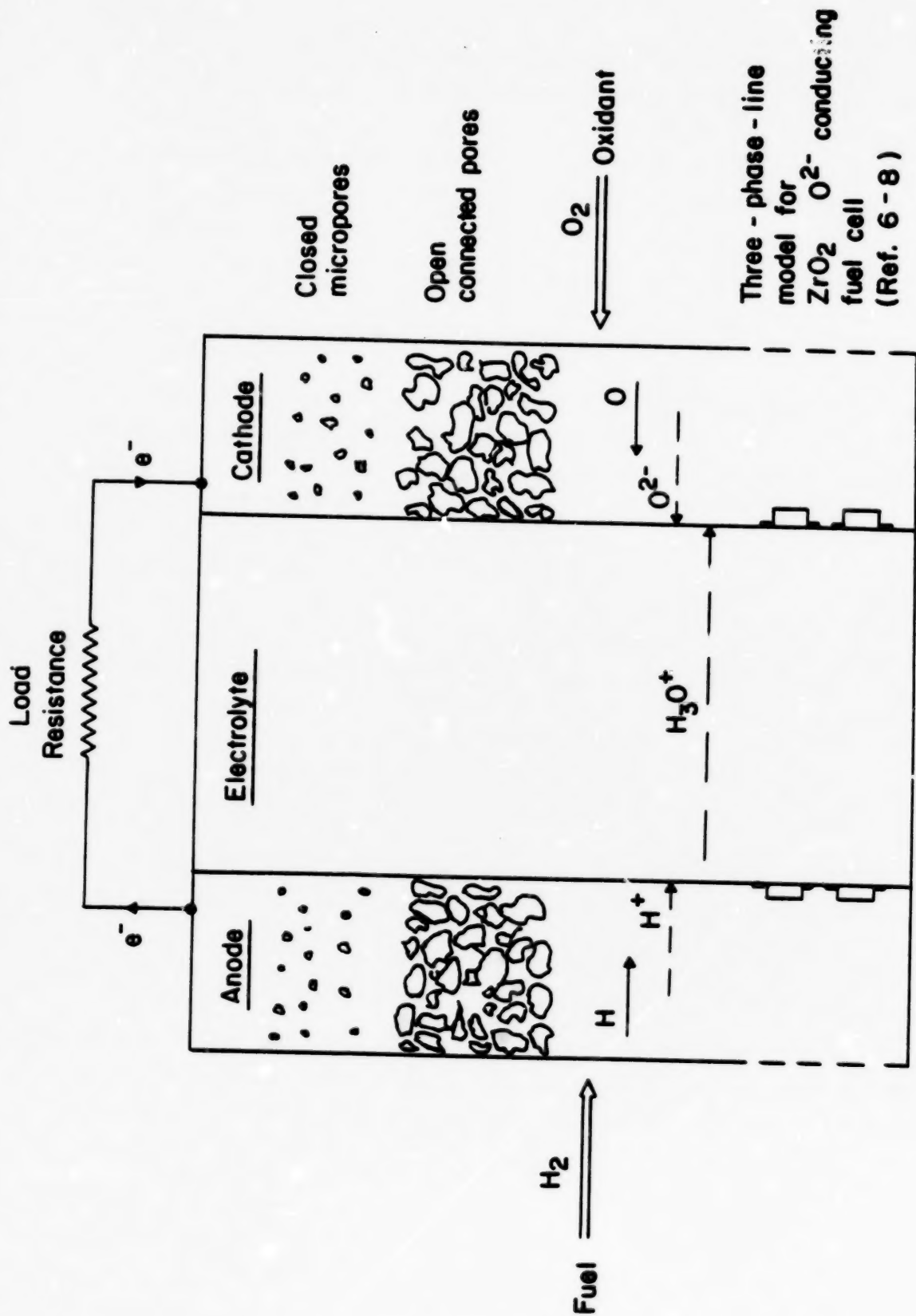


Fig. 1. Schematic view of protonic fuel cell electrode porosity and the three-phase-line model

Electrolyte

- a) Adsorption and dissociation of species on electrolyte surface.
- b) Surface diffusion of adsorbed species on electrolyte to three-phase boundary.
- c) Dissolution of adsorbed species into electrolyte bulk.
- d) Bulk and/or grain boundary electric-field migration of dissolved species in electrolyte.

Interface

- a) Charge transfer across the electrode/electrolyte two-phase boundary.

Fuel cell electrode characteristics can be described both in terms of their polarization properties and their morphologies. Concentration polarization is caused by diffusion-limitation processes, which have been explained (5,9) by Fick's law

$$J_m = D \frac{dC}{dx} \quad (1)$$

where J_m is the molar flux, D is the diffusion coefficient, and dC/dx is the concentration gradient. For ideal gases (12),

$$J_m = \frac{D}{RT} \frac{dP}{dx} \quad (2)$$

The terms R , T , and P are the gas constant, absolute temperature, and pressure, respectively. The current density is then given by (5,12)

$$J_d = nF J_m \quad (3)$$

where n is the number of charges per reactant gas molecule, and F is Faraday's constant. Depending on the nature of the process, the diffusion constant will have different meanings. Diffusion in the bulk electrode

material (5) involves the bulk coefficient, D_B . Diffusion through a porous structure (13) requires description by the Knudsen flow constant, D_K ; here, the molar flux is also multiplied by the per cent porosity, p , of the electrode material. Diffusion along the three-phase-line (6-8) is described by the surface diffusion coefficient, D_S .

Activation polarization is related to charge transfer and electrocatalytic processes at the electrode-electrolyte interface, which can be modelled (8,14) by the Butler-Volmer equation

$$J_c = J_0 [\exp(1-\beta)VF/RT - \exp(-\beta VF/RT)] \quad (4)$$

Here, J_0 is the exchange current density, β is the transfer coefficient, and V is the overpotential.

ELECTRODE PROPERTIES

MORPHOLOGICAL PARAMETERS AND MEASUREMENT METHODS

In order to characterize the properties of fuel cell electrodes, it is first necessary to define these properties in a manner such that they can be measured with physical and chemical significance. It will be assumed that the electrode composition, e.g., Pt, Ni or LaCoO_3 , generally satisfies the criteria (15) of chemical stability, mechanical stability, electrocatalytic activity and economic feasibility. These parameters and their methods of measurement are given in Table 1. Also shown for each parameter are the appropriate electrode selection criterion and the type of polarization considered to be most important.

THIN-FILM POROSITY MEASUREMENTS

The most common use (16) of thin-film devices occurs in the area of microelectronics. Integrated circuits are composed of Si-SiO₂ MOS (metal-oxide-semiconductor) systems in which the oxide layer is typically 100 nm in thickness. Capacitors are often fabricated from Ta₂O₅ films. It is necessary that these dielectric layers be excellent electronic insulators; hence, defects such as porosity cannot be tolerated. The absence of porosity in thin film is evidenced by their performance and lifetime. However, microporosity has been measured for some cases in thin films, and typical results are shown in Tables 2 and 3.

Table 1. Electrode morphology characteristics

<u>Electrode Morphology Parameter</u>	<u>Measurement Method</u>	<u>Electrode Selection Criterion</u>	<u>Polarization Type</u>	<u>Reference</u>
Thickness	Stylus instrument, Rutherford backscattering spectrometry (RBS) if thickness $< 1 \mu\text{m}$	Electrochemical Activity	Concentration	Badwal and (11) de Bruin (1982)
Bulk density	Gravimetric and thickness data	Electrochemical Activity	Concentration	(8) Verkerk et al. (1983)
Porosity	Mass density, Mercury porosimeter	Electrochemical Activity	Concentration	(17) Innes
Particle size distribution	Particle size analyser	Electrochemical Activity	Concentration and Activation	(17) Innes
Specific surface area	Brunauer, Emmett, and Teller (BET) method	Electrochemical Activity	Activation	(17) Innes
Adsorption	Langmuir isotherm	Electrochemical Activity	Activation	(14) Wang and Nowick (1979)
Three-phase line; Electrode, electrolyte, and gas contact areas	Scanning electron microscope (SEM) method	Electrochemical Activity	Concentration and Activation	(8) Verkerk et al. (1983)
Electronic resistivity	Four-point probe	Electrochemical Activity	Ohmic	(8) Verkerk et al. (1983)
Chemical and thermal stability	Thermogravimetric method; Auger Electron Spectroscopy (AES)	Chemical Stability	-	(18) Kononyuk (1983) Ray et al. (1983)
Mechanical stability	Stress; Thermal expansion	Mechanical Stability	-	(19) Ray et al. (1983) (18) Kononyuk (1983)

Table 2. Porosity of thin films

Composition	Deposition Method	Film Thickness (μm)	Porosity Measurement Method	Porosity (%)	Reference
Permalloy 80% Ni, 20% Fe	Evaporation	0.10 - 0.16	Density	0 - 12	(20) Yamanaka and Ueda (1966)
SiO_2 , MgF_2 , SrF_2 , ZnS	Evaporation	0.05 - 0.3	Spectroscopic	0.5 - 14	(21) Pervsev, Muranova, and Zolotarev (1973)
Al_2O_3	Sputter	Not given	Hydrostatic Density	2 - 10	(22) Sokolova, Kozlova, Derko, and Kiiiko (1973)
Ni	Evaporation	3 - 9	Hydrostatic Density	4.7 - 5.2	(23) Fuks, Cheremskoy, Nechitsaylo, Federenko, and Demerskiy (1975)
Ni	Evaporation	8	Hydrostatic Density	0.0 - 0.2	(24) Fuks, Cheremskoy, Belozorov, Chuvurina, and Koshchenko (1982)

Table 2 (cont.)

$\text{Ga}_2\text{O}_3 + \text{As}_2\text{O}_3$	Anodization	0.1 - 0.6	Density and Rutherford Backscattering Spectrometry	Bulk density; negligible porosity	(16) Canada (1983)
Al, V	Evaporation	0.02 - 0.1	Density and Rutherford Backscattering Spectrometry	Bulk density; negligible porosity	(25) Canada; (1981)
Nb, Ta	Sputter	0.005 - 0.03	Density and Rutherford Backscattering Spectrometry	Bulk density; negligible porosity	(25) Canada (1981)

Table 3. Pore diameter of thin films

Composition	Deposition Method	Film Thickness (μm)	Pore Diameter Measurement Method	Pore Diameter (μm)	Reference
Pt	Pt paste	Not given	SEM	0.01 - 1	(13) Pizzini, Bianchi Colombo, and Torchio (1973)
Ni	Gas discharge	0.1	SEM	0.06	(26) Troyan and Bykov (1977)
Au	Evaporation	0.1	TEM	0.005	(27) Lloyd and Nakahara (1977)
Cu-Au	Electron gun evaporation	1 - 10	SEM	0.25 - 1	(28) Feinstein and Bindell (1979)

THIN-FILM SURFACE AREA MEASUREMENTS

In addition to porosity, the specific surface area of thin films has been measured. Examples of these results are given in Table 4. This property is important in catalytic devices because a large surface area per unit mass of material is required for effective catalysts.

Table 4. Specific surface area of thin films and catalysts

Composition	Deposition Method or Catalyst Preparation Technique	Film Thickness (μm) or Catalyst Description	Surface Area Measurement Method	Specific Surface Area (m^2/g)	Reference
$\text{Al}_2\text{O}_3\text{-SiO}_2$	Calcined oxides	Catalyst sample	BET	100-700	(17) Innes (1968)
Ti	Evaporation	0.005-0.1	BET	23	(29) Singh and Surplise (1972)
Polymeric Catalyst Support	Polymerization	Porous beads 0.25-1 μm diameter, 1-70% porous	not given	10-24	(30) Lieto, Miletein, Albright, Minkiewicz, and Gates (1983)
V_2O_5	Reduction of V_2O_5	Catalytic sample	BET	9	(31) Miyamoto, Hattori, and Murakami (1983)

PROPERTIES OF THIN FILM CATALYSTS, AND FUEL CELL ELECTRODES

From Tables 2, 3, and 4, it is evident that electrodes for solid electrolyte fuel cells exhibit properties that are characteristic of both thin films and of catalysts. These similarities can also be seen by comparing the requirements of the three types of devices, and this comparison is presented in Table 5.

It would appear from Table 5 that attempts to produce catalytically active fuel cell electrodes by utilizing thin-film technology exclusively may not result in optimum performance due to the general lack of porosity and low specific surface area found for those devices. However, because electrode thickness on the micrometer scale is not a physical limitation to the fuel cell design, thicker and more porous structures may prove to be superior to thin-film electrodes. Differences in electrode performance will be evident from polarization measurements.

Table 5 - Comparison of thin film, catalyst and electrode requirements

Requirement	Thin Film in MOS Device	Catalyst	Solid Electrolyte Fuel Cell Electrode
Thickness	$\approx 1 \mu\text{m}$	$\gg 1 \mu\text{m}$	$\approx 1 \mu\text{m}$
Porosity	Minimum	Maximum	Maximum
Specific Surface Area	Approximately same as geometric area	10-1000 m^2/g	$\geq 10 \text{ m}^2/\text{g}$
Charge Transfer	Yes, at the Semiconductor- oxide interface; No, at the metal-oxide interface	Yes	Yes
Catalysis	No	Yes	Yes
Gas Flow	No	Yes	Yes
Adhesion to Substrate	Yes	Yes, for substrates coated with catalysts	Yes
Subject to Thermal cycling	Yes	Yes	Yes
Subject to Chemically Reactive Environment	No	Yes	Yes
Conversion Efficiency	Not defined	Defined by ratio of products to reactants	Defined by ratio of electronic current to gas molar flux for diffusion

ELECTRODES FOR ZrO_2 -TYPE FUEL CELLS

The major portion of research and development in the area of solid-electrolyte fuel cells has been conducted on ZrO_2 -type systems. These electrolytes are ionically conductive through the process of oxygen ion migration and the cells are typically operated in the temperature range of 800-1000°C.

Table 6 summarizes, in chronological order, the major results obtained for various electrode configurations. Early findings (3-5) have also been tabulated and compared. It can be seen that the electrode material most commonly used was platinum. Paste and sputtered electrodes have been made porous by the simultaneous application of heat and electrical current. The morphology has generally been described in terms of porosity and thickness, but more complete evaluations were often not presented. The rate-determining step, i.e., the slowest process, has been indicated where possible. Conflicting results were attributed (5) to a change in the rate-determining step with changes in temperature, gas pressure, morphology, or time.

Table 6. Electrode of ZrO_2 -type fuel cells

Electrolyte Type	Working Electrode	Electrode Composition	Electrode Preparation Method	Electrode Morphology	Electrode Morphology Evaluation Method	Rate-Determining Step or Polarization Type	Reference
ZrO_2	Cathode	Pt	Pt wire	Point contact	Not given	Surface diffusion of oxygen atoms on ZrO_2	(32) Karpachev, Filajev, and Palguyev (1964)
ZrO_2	Cathode	Pt	Pt wire	Point contact	Not given	Surface diffusion of oxygen	(33) Kleitz (1968)
ZrO_2	Anode	Pt	Pt from chloroplatinic acid heated to 600-700°C	Porous	Not given	Concentration polarization	(34) Guillon, Millet and Palous (1968)
ZrO_2	Cathode	Pt	Pt paste or sputtered Pt; Porosity from current treatment	Porous	Capillary action	Dissociation of O_2 or electron transfer	(35) Bauerle (1969)
ZrO_2	Anode	Ni	Not given	Porous	Not given	Gives ratio of activation and concentration polarizations	(36) Tedmon, Spacil, and Mitoff (1969)
ZrO_2	Cathode	Perovskites	Applied from slurry	Porous 0.1 mm thick	Not given	Concentration polarization	(36) Tedmon, Spacil, and Mitoff (1969)
ZrO_2	Cathode	Pt	Pt paste heated to 800°C	Porous	Not given	At low voltages, diffusion of oxygen atoms is rate limiting. At high voltages, adsorption of oxygen atoms is rate limiting.	(9) Yanagida, Brook, and Kroger (1970)

Table 6 (Cont.)

ZrO ₂	Cathode	Pt	Pt from chloroplatinic acid heated to 600-700°C, then heated to 1100°C	Porous	Not given	For Ar-O ₂ mixtures, diffusion overpotential limits the current. The limiting currents, proportional to the oxygen pressures, are controlled by diffusion of gaseous oxygen in the pores of the Pt electrode.	(10) Etsell and Flengas (1971)
ZrO ₂	Cathode	Pt	Pt paste	Porous	Not given	Not available	(37) Schouler (1972)
ZrO ₂	Cathode	Pt	Chloroplatinic acid or Pt paste heated at 600°C then up to 1000°C	Porous	SEM; Pore size estimation	Activation polarization due to oxygen adsorption and dissociation	(13) Pizzini, Bianchi, Colombo, and Torchio (1973)
ZrO ₂	Cathode	Pt	As above	Porous	Not given	Surface diffusion of oxygen atoms on Pt	(38) Pizzini, Bianchi, Corradi, and Mari (1974)
ZrO ₂	Cathode	NIPT ₂ O ₄	Metal nitrates deposited and heated to 500°C	Porous	SEM	Reversible behaviour up to 100 mA/cm ² at 5 x 10 ⁻² bar, 850°C	(4) Mari, Scolari, Fiori, and Pizzini (1977)

Table 6 (Cont.)

CeO_2	Anode and Cathode	Pt	Engelhard 6080 (fluxed) or 6926 (unfluxed) Pt paste heated at 800°C for 4 h	Porous	SEM	At high oxygen pressures. (14) Wang and Nowick (1979) V-I curves obey the Butler-Volmer equation with transfer coefficients of unity. This result implies a charge transfer (activation) mechanism. Oxygen for the charge transfer process is supplied through adsorbed atoms on the Pt electrode surface, obeying a Langmuir isotherm.
CeO_2	Anode and Cathode	Pt	As above	Porous	Not given	At low oxygen pressures the limiting current is characteristic of concentration polarization. Coarser electrodes also lead to diffusion effects. (39) Wang and Nowick (1979)
CeO_2	Anode and Cathode	Pt	As above	Porous	Not given	Impedance results consistent with (14) Wang and Nowick (1979) (6) Wang and Nowick (1981)
ZrO_2	Cathode	Pt	Sputtered Pt, 1 μm thick, porosity from current treatment	Porous	Not given	Gas phase polarization at high overvoltages, ohmic behavior at moderate overvoltages, diffusion and charge control at low overvoltages. (41) Gur, Ralstrick, and Huggins (1979)
ZrO_2	Anode	Pt	Engelhard 6926 (unfluxed) Pt paste and Au paste	Porous	Not given	Similarity of V-I results (42) Ong, Chiang and Mason (1981) for porous Pt and Au electrodes established importance of the electrolyte surface in the electrocatalytic process.

Table 6 (Cont.)

ZnO_2	Cathode	Pt	Pt wire	Point contact	-	Not given	(43) Isaacs, Olmer, Schouler, and Tank (1981)
ZnO_2	Cathode	Pt	Pt wire	Point contact	-	Not given; Kismuth impurity found in Engelhard 6082 fused paste.	(44) Olmer and Isaacs (1982)
CuO_2	Cathode	Pt	Engelhard 6082 (fused) Pt paste heated 1000°C for 96 h, and cooled to 1 h	Point contact	52M	In the oxygen pressure range of 10^{-4} atm., the current became limited at a value proportional to the pressure. This limitation was explained in terms of a gas diffusion mechanism.	(1) Braunschtein, Tannhauser, and Rieck (1981)
ZnO_2	Cathode	Pt	An above	Point contact	Not given	Similar to results of Braunschtein et al. (1981)	(45) Braunschtein, Tannhauser, and Rieck (1981)
ZnO_2	Cathode	Pd	Sputtered Pd 400 nm thick heated to 1100°C for 96 h	Point contact	52M	Not given	(11) Arduini and de Bruijn (1982)

Table 6 (Cont.)

ZrO_2 , Bi_2O_3 and CaO_2	Cathode	Pt	Sputtered Pt 150 nm thick heated to 1200-1400°C for 2-4 h. Also Pt gauze	Forma	SEM Three-phase line length, and interface surface area	The combination of electrolyte and elec- trode materials determines whether the dominating absorption or diffusion step occurs on the elec- trolyte or on the elec- trode.	(8) Verkerk, Hamming, and Burggraaf (1983)
						For ZrO_2 and CaO_2 , the oxygen atoms for the electrode process are supplied by dissociative adsorption of O_2 at the Pt electrode followed by transport to the reaction site where charge transfer occurs. For Bi_2O_3 , the adsorption and diffusion steps occur on the elec- trolyte.	
						The electrode resistance for electrodes with the same morphology is much higher for ZrO_2 and CaO_2 than for Bi_2O_3 .	

Table 6 (Cont.)

ZrO_2 , Ba_2O_3 and Ce_2O_3	Cathode	Pt	As above	Porous	Not given	For low oxygen pressures gas diffusion is the rate-limiting process. For high oxygen pressures charge transfer is the rate-limiting step.	(46) Verkerk and Burggraaf (1983)
ZrO_2	Cathode (Oxygen sensor)	Pt, Ni, Mo	RF sputtering	Pt layer, 1 μm YSZ, 150 nm Ni, and 200 nm Mo on Si substrate	Not given	Sputtering deposition, mechanical stress, thermal stability from Auger electron spectroscopy	(19) Ray, Greene, Polack, and Welsh (1983)
ZrO_2	Cathode	LaCoO ₃ LaCrO ₃ PrCoO ₃ PrCrO ₃	Acetylene flame spray	Porous 75-150 μm thick	Not given	Not given	(47) Ohno, Nagata and Sato (1981)
ZrO_2	Cathode (oxygen sensor)	Sr doped LaCrO ₃	Hydroalcoholic solution	Homogeneous; large specific surface area; no open porosity; 2 μm thick	Not given	Not given	(48) Barbi, Castraghi, and Mari (1983)

ELECTRODES FOR PROTONIC ELECTROLYTE FUEL CELLS

Electrolytes of primary concern in the CANMET hydrogen-air fuel cell program are protonically conductive ceramics. Ionic species such as hydronium, H_3O^+ , are mobile at temperatures $\sim 300^\circ\text{C}$ in these materials. These temperatures are considerably less than those required for the ZrO_2 cell. This lowering of the operating temperature results in two important advantages relative to the ZrO_2 system: (i) higher theoretical efficiency; and (ii) less severe thermal environment. A further distinction between these cells is that the protonic electrolyte requires an ion exchange (50) step while the ZrO_2 type electrolyte does not. During operation, water is formed at the cathode of the protonic cell, whereas for the ZrO_2 cell it is formed at the anode.

Table 7 suggests compositions and morphology measurements for electrodes on protonic electrolytes. Initially, both the anode and the cathode should be platinum in paste or sputtered form. These electrodes will serve as standards and will also be important for characterizing the electrolyte. Subsequent experiments (15) should be concerned with the morphology and polarization properties of non-noble metals and oxides as electrode materials.

Table 7. Suggested electrode studies for protonic electrolytes

Electrolyte Type	Working Electrode	Electrode Composition	Electrode Preparation Method	Electrode Morphology	Electrode Morphology Evaluation Method	Reference
Protonically Conducting	Anode	Pt	Pt paste and heat treatment	Porous	SEM, porosity, surface area, DC polarization	6,7,9,13,14,35,37,42,45
		Pt	Sputtered Pt and heat treatment	Porous	As above	8,11,41,46
		Ni	Sputtered Ni and heat treatment	Porous	As above	36
		LaNi ₅	Sputtered LaNi ₅ and heat treatment	Porous	As above	49
Protonically Conducting	Cathode	Pt	Pt paste and heat treatment	Porous	As above	6,7,9,13,14,35,37,42,45
		Pt	Sputtered Pt and heat treatment	Porous	As above	8,11,41,46
		Semiconducting oxides e.g., In ₂ O ₃	Sputtering	Porous	As above	15,36
		Perovskites e.g., LaCoO ₃	Sputtering, slurry, solution, etc.	Porous	As above	47,49

SUMMARY AND CONCLUSIONS

Electrode morphology parameters can be defined in terms of measurable quantities. Their usefulness will depend to a large extent upon the reproducibility of these quantities. The parameters can also be associated with electrode material selection criteria and type of polarization. Sputtered thin films are characteristically non-porous as porosity is detrimental to the operation of planar-technology electronic devices. However, some thin films, TiO_2 for example, exhibit specific surface areas of $\approx 20 \text{ m}^2 \text{ g}^{-1}$. A comparison of thin-film, catalyst, and electrode requirements indicates that these devices have similar properties. Studies of ZrO_2 fuel cells show that the polarization characteristics are related to electrode morphology.

By comparing morphology models with experimental results, a better understanding of fuel cell electrode processes will be obtained. The rate-determining step of highly porous electrodes will be activation polarization involving catalytic steps occurring at the interface. Slightly porous electrodes will be limited by the rate of gas diffusion (or concentration polarization) through the structure. It is anticipated that these studies will also improve overall cell performance.

The analysis presented here has specific relevance to the development of electrodes for protonically conducting solid electrolytes. Subsequent to the selection of candidate electrode composition, it will be necessary to determine the best electrode deposition method. Processes such as paste application, sputtering, spraying, slurry deposition, and chemical deposition can be evaluated by measuring the electrode morphology characteristics and polarization.

REFERENCES

1. McDougall, A. "Fuel cells"; John Wiley and Sons, New York; 1976.
2. Noyes, R. "Fuel cells for public utility and industrial power"; Noyes Data Corporation, Park Ridge, New Jersey; 1977.
3. Steele, B.C.H. "High temperature fuel cells and electrolyzers"; In: "Electrode processes in solid state ionics"; M. Kleitz and J. Dupuy (Eds), D. Reidel Publ. Co., Dordrecht, Holland; 1976.
4. Mari, C., Scolari, V., Fiori, G. and Pizzini, S. "Structural, electrical, and electrochemical characterization of Ni-Pr oxide thick films"; J Appl Electrochem 7:95;1977.
5. Gur, T.M., Raistrick, I.D. and Huggins, R.A. "Steady-state D-C polarization characteristics of the O₂ Pt/stabilized zirconia interface"; J Electrochem Soc 127:2620; 1980.
6. Wang, DaYu and Nowick, A.S. "Diffusion-controlled polarization of Pt, Ag and Au electrodes with doped ceria electrolyte"; In: J Electrochem Soc 128:55; 1981.
7. Braunshtein, D., Tannhauser, D.S. and Riess, L. "Diffusion-limited charge transport at platinum electrodes on doped CeO₂"; J Electrochem Soc 128:82; 1981.
8. Verkerk, M.J., Hammink, M.W.J. and Burggraaf, A.J. "Oxygen transfer on substituted ZrO₂, Bi₂O₃ and CeO₂ electrolytes with platinum electrodes"; J Electrochem Soc 130:70; 1983.
9. Yanagida, H., Brook, R.J. and Kroger, F.A. "Direct current-voltage characteristics of calcia stabilized zirconia with porous platinum electrodes"; J Electrochem Soc 117:593; 1970.
10. Etsell, T.H. and Flengas, S.N. "Overpotential behaviour of stabilized zirconia solid electrolyte fuel cells"; J Electrochem Soc 118:1890; 1971.
11. Badwal, S.P.S., de Bruin, H.J. "Electrode kinetics at the palladium/ceramic oxide electrolyte interface"; J Electrochem Soc 129:1921;1982.
12. Schouler, E.J.L., Birchall, M.L.S., and Lundsgaard, J.S. "Porous electrodes for solid electrolyte systems"; In: "Solid state protonic conductors 1"; J. Jensen, M. Kleitz (Eds), Odense University Press, Odense, Denmark; 1982.

13. Pizzini, S., Bianchi, M., Colombo, P. and Torchio, S. "On the influence of the annealing temperature and heavy current treatments on the porous structure of platinum electrodes and in the kinetics of the oxygen reaction at high temperatures"; J Appl Electrochem 3:153;1973.
14. Wang, D.Y., and Nowick, A.S. "Cathodic and anodic polarization phenomena at platinum electrodes with doped CeO_2 as electrolyte I. Steady-state overpotential"; J Electrochem Soc 126:1155; 1979.
15. Canaday, J.D., Kuriakose, A.K., Ahmad, A. and Wheat, T.A. "Electrode materials for protonically conducting solid electrolyte fuel cells"; Division Report ERP/MSL 83-120 (IR); CANMET, Energy, Mines and Resources Canada; 1983.
16. Canaday, J.D. "Ionic transport studies of anodic GaAs and GaAs/metal layer oxides"; Ph.D. Thesis, University of Guelph; 1983.
17. Innes, W.B. "Determination of surface area and pore structure of catalysts"; In: "Experimental methods in catalytic research"; R.A. Anderson (Ed.), Academic Press, New York; 1968.
18. Kononyuk, I.F., Tolochko, S.P., Lutsko, V.A. and Anishchik, V.M. "Preparation and properties of $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$, ($0.2 \leq x \leq 0.6$)"; J Solid State Chem 48:209; 1983.
19. Ray, M.A., Greene, J.E., Polack, A.J. and Welsh, L.B. "Summary abstract: Rf-sputter-deposited multilayer thin film oxygen sensors"; J Vac Sci Tech A 1:2:322; 1983.
20. Yananaka, M. and Ueda, R. "Porosity and coercive force in evaporated thin films"; J Phys Soc Japan 21:1607; 1966.
21. Perveev, A.F., Muranova, G.A. and Zolotarev, V.M. "Spectroscopic method for determining the sorption and porosity properties of thin solid films"; Soviet Physics-Solid State 14:2510; 1973.
22. Sokolova, T.V., Kozlova, I.R., Derko, Kh. and Kiiko, A.V. "How certain physicochemical properties of plasma-deposited aluminum oxide depend on the deposition conditions"; Izv Akad, Nauk SSSR Neorg Mater 9:611; 1973.
23. Fuks, M.Ya., Cheremskoy, P.G., Nechitaylo, A.A., Federenko, A.I. and Demerskiy, V.V. "Influence of annealing on the stability of macro- and microporosity in condensed films"; Fiz Metal Metalloved 39:72; 1975.

24. Fuks, M. Ya., Cheremskoy, P.G., Belozarov, V.V., Chuvurina, S.N. and Roshchenko, S.T. "Influence of isothermal and thermal cycling treatments on the porosity and internal stresses in nickel films and coatings"; Fiz Metal Metalloved 53:44; 1982.
25. Canaday, J.D. Unpublished data; 1981.
26. Troyan, V.A. and Bykov, V.N. "The development of porosity in Ni films bombarded with He^+ and N^+ ions"; Thin Solid Films 42:139; 1977.
27. Lloyd, J.R. and Nakahara, S. "Voids in thin As deposited gold films prepared by vapor deposition"; J Vac Sci Tech 14:655; 1977.
28. Feinstein, L.G. and Bindell J.B. "The failure of aged Cu-Au thin films by Kirkendall porosity"; Thin Solid Films 62:37; 1979.
29. Singh, B. and Surplice, N.A. "The electrical resistivity and resistance-temperature characteristics of thin titanium films"; Thin Solid Films 10:243; 1972.
30. Lieto, J., Milstein, D., Albright, R.L., Minkiewicz, J.V. and Gates, B.C. "Polymeric supports for catalysts"; Chemtech, Jan. 1983.
31. Miyamoto, A., Hattori, A. and Murakami, Y. "The concentration of surface V=O species on oxidized vanadium oxide catalysts"; J Solid State Chem 47:373; 1983.
32. Karpachev, S.V., Filajev, A.T. and Palguyev, S.F. "Polarization of carbon monoxide electrodes on platinum in a solid zirconia-lime electrolyte"; Electrochem Acta 9:1681; 1964.
33. Kleitz, M. Thesis, University of Grenoble; 1968.
34. Guillou, M., Millet, J.M. and Palous, S. "Reactions electrochimiques d'echange d'oxygene entre un oxyde semi conducteur et des gas non-ionises et faiblement ionises"; Electrochim Acta 13:1411; 1968.
35. Bauerle, J.E. "Study of solid electrolyte polarization by a complex admittance method"; J Phys Chem Sol 30:2657; 1969.
36. Tedmon Jr., C.S., Spacil, H.S. and Mitoff, S.P. "Cathode materials and performance in high temperature zirconia electrolyte fuel cells"; J Electrochem Soc 116:1170; 1969.
37. Schouler, E. Thesis, University of Grenoble; 1972.
38. Pizzini, S., Bianchi, M., Corradi, A. and Mari, C. J Appl Electrochem 4:7; 1974.

39. Wang, Da Yu and Nowick, A.S. "Cathodic and anodic polarization phenomena at platinum electrodes with doped CeO_2 as electrolyte"; In: J Electrochem Soc 126:1166; 1979.
40. Wang, Da Yu and Nowick, A.S. "Polarization phenomena associated with reduction of a doped ceria electrolyte"; In: J Electrochem Soc 127:113; 1980.
41. Gur, T.M., Raistrick, I.D. and Huggins, R.A. "Solid electrolyte/porous electrode kinetics"; In: "Fast ion transport in solids", P. Vashista, Mundy and Shenoy (Eds.), Elsevier North Holland Inc.; 1979.
42. Ong, B.G., Chang, C.C. and Mason D.M. "Electrocatalytic role of stabilized zirconia on the anodic current-overpotential behavior in hydrocarbon fuel cells"; Solid State Ionics 3:4:447; 1981.
43. Isaacs, H.S., Olmer, L.J., Schouler, E.J.L. and Yank, C.Y. "Electrode reactions at solid oxide electrolytes"; Solid State Ionics 3:4:503; 1981.
44. Olmer, L.J. and Isaacs, H.S. "The effect of electrode surface impurities on the oxygen electrode reaction at zirconia electrolytes"; J Electrochem Soc 129:345; 1982.
45. Braunshtein, D., Tanhouser, D.S. and Riess, I. "Diffusion-limited charge transport at platinum electrodes on doped CeO_2 "; Solid State Ionics 3:4:509; 1981.
46. Verkerk, M.J. and Burggraaf, A.J. "Oxygen transfer on substituted ZrO_2 , Bi_2O_3 and CeO_2 electrolytes with platinum electrodes"; J Electrochem Soc 130:78; 1983.
47. Ohno, Y., Nagata, S., and Sato, H. "Effect of electrode materials on the properties of high-temperature solid electrolyte fuel cells"; Solid State Ionics 3:4:439; 1981.
48. Barbi, G.B., Casiraghi, A. and Mari, C.M. "Electrode material for high-temperature oxygen partial pressure electrochemical sensors: strontium-doped lanthanum chromite"; Rev Sci Instrum 54:486; 1983.
49. Jensen, J. "Materials requirements targets and applications"; In: "Solid state protonic conductors I", J. Jensen and M. Kleitz (Eds.), Odense University Press, Odense, Denmark; 1982.
50. Bell, M.F. and Sayer, M. "The development of ceramic proton conductors"; DSS Contract No. OS481-00440 for the Department of Energy, Mines and Resources, CANMET, Ottawa, Canada.

POOR

QUALITY

ORIGINAL

